who found $k = 10^{126} \exp(-115.7/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction

$$\text{NH}_3 + \text{NO}_2 \rightarrow \text{NH}_2 + \text{HNO}_2 \quad (10)$$

From the vapor-pressure measurements of Feick, we can estimate the concentration of ammonia in our capillary tubes and calculate the concentration of nitrogen dioxide required to consume ammonia by eq 10 at the initial rate that we observe. For a temperature of 370°C and a capillary containing $5 \times 10^{-3}$ mol of ammonium nitrate in a volume of $4 \times 10^{-5}$ L we find an initial rate of $6 \times 10^{-6}$ mol/s ($k = 0.12 \text{ s}^{-1}$). The initial rate of eq 7 at 370°C with $[\text{NH}_3] = 0.057 \text{ M}$ and $V = 4 \times 10^{-5}$ L is $3.1 \times 10^{-4} \text{[NO}_2\text{]} \text{ mol/s}$. A match of rate requires $[\text{NO}_2] = 2 \text{ M}$. By trial we have found that nitrogen dioxide at a concentration of 0.05 M in a capillary tube shows a distinct red-brown color. According to our visual observations and color video recordings, however, the nitrogen dioxide is either absent or on the threshold of visibility throughout the decomposition reaction. It appears that eq 10 is too slow to account for the main reaction, but it could perhaps be involved in the side reaction leading to N₂. The absence of a primary H/D kinetic isotope effect is also evidence against its participation. One final point is that reaction 10 is the slow step in the sequence of reactions and its activation energy is 116 kJ/mol. It would be difficult to account for the observed $E_{\text{act}}$ of 193 kJ on this basis.

**Trapping of Intermediates.** Ammonium nitrate was decomposed in the presence of toluene in the high-temperature regime (340°C) in an effort to trap and identify reactive intermediates. The two most abundant products were benzaldehyde and phenylnitromethane followed by nitrobenzene, benzyl alcohol, and benzonitrile. It seems clear that hydrogen atoms are abstracted from toluene to form benzyl radicals, which combine with NO₂ to form phenylnitromethane and with some other oxygen-containing intermediate to form benzyl alcohol. Benzaldehyde probably results from further oxidation of benzyl alcohol. Benzonitrile is probably the dehydration product of phenylnitrosomethane via benzaldehyde oxime. The origin of nitrobenzene is unclear. It is interesting that 2- and 4-nitrotoluene, the normal products of reaction of toluene with nitronium ion, are absent.

**Conclusion.** Various lines of evidence indicate that the well-established ionic mechanism for decomposition of ammonium nitrate at temperatures below 300°C is supplanted by a rate-controlling homolysis of nitric acid at higher temperatures. The observed activation energy changes continuously from 118 kJ at low temperature to 193 kJ at high temperature. The enthalpy of homolysis of nitric acid is nearly equal to the latter. The change of $E_a$ strongly implies a change of mechanism, although it does not prove it conclusively. At the highest temperatures it appeared that ammonium nitrate in large containers was completely vaporized and yet gave the same products at the same rate as in small tubes containing liquid ammonium nitrate. Reaction in the vapor phase could not occur by the ionic mechanism. Added H₂O, NH₃, and HONO₂ strongly influence the rate at low temperatures because of their effects on nitronium ion concentration, but the effects fade out at high temperature. N₂O₅ shows no primary kinetic isotope effect at high temperature. This is appropriate to homolysis of HONO₂ but inappropriate to a chain reaction involving NH₃ and NO₂. The presence of radical intermediates was demonstrated by trapping with toluene as scavenger.

**Acknowledgment.** This work was supported by the Research Center for Energetic Materials, an NSF/Industry cooperative venture.

Registry No. NH₄NO₃, 6484-52-2; Dₙ, 7782-39-0; H₂O, 7732-18-5; NH₃, 7664-41-7.

**Excitation of IF(B³Π₉⁻) by Active Nitrogen**

Lawrence G. Piper* and William J. Marinelli

Physical Sciences Inc., Research Park, P. O. Box 3100, Andover, Massachusetts 01810

(Received: August 4, 1988; In Final Form: November 23, 1988)

Active nitrogen, or the effluents of microwave discharges in flowing N₂/Ar or He mixtures, excites IF(B³Π₉⁻) strongly in a discharge-flow apparatus. The distribution of IF(B) vibrational levels in helium is characterized roughly by an 1150 K Boltzmann temperature and is somewhat hotter in an argon buffer. Excitation rates are as high as $1 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Species such as $\text{N}(^3\text{D}), \text{N}(^3\text{P}), \text{N}_2(\text{A}_3\Sigma^+_u),$ and $\text{N}_2(\text{a}_1\Sigma^+_u)$ are too low in number density to account for the observed excitation rates. We conclude, therefore, that the IF is excited by $\text{N}_2(X,e^0)>9$, a species that is abundant in the flow.

**Introduction**

The molecule IF and other interhalogens have been the subject of considerable interest in recent years because their compressed electronic energy manifold and intense radiative transitions make them ideal candidates for visible molecular lasers. Clyne and co-workers studied the radiative and collisional properties of IF, BrCl, and BrF, and showed that these species were highly suitable for forming an electronic transition laser operating on the Br(B¹Π₉⁻) → X(^1Σ⁺) transition because the upper states have short radiative and long electronic-quenching lifetimes. Davis and Hancock excited ground-state IF, formed in an IF/F₂ flame, with a pulsed dye laser and demonstrated optically pumped lasing action on the IF(B→X) transition. Efficient chemical (kinetic) means for pumping the IF(B) state remain to be determined.

*Author to whom correspondence should be addressed.

strongly. This excitation is even more robust when the ground electronic state of IF is vibrationally excited. Davis and co-workers observed IF(B) excitation when the effluents of microwave discharges in He/N2 mixtures interacted with the I2/F2 mixing zone of their reactor. This excitation was much stronger than they had observed from singlet-oxygen excitation. They did not identify which species in their active nitrogen was responsible for the IF excitation but speculated it might be the A3Z+, crowave discharges in He/N2 mixtures interacted with the 12/F2 workers12 observed IF(B) excitation when the effluents of metastable nitrogen species and ground-state N2, and produced c" = 0-6 with about equal probability. The vibrational distribution relaxes rapidly, however, in collisions with the reactor bath gas even at pressures of a few Torr. We found the vibrational relaxation rate coefficients for levels 3-6 to about 3 \times 10^{12} \text{cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}. More extensive measurements by Wolf and Davis on IF(B) vibrational relaxation confirmed these findings.14 Although we did not study it explicitly, electronic quenching of IF(B) in our reactor must have been much slower because we observed strong IF(B) excitation by N2(A) at pressures up to 10 Torr. Wolf and Davis also corroborate the less efficient electronic quenching of IF(B).15

Figure 1. Flow-tube apparatus for studying reactions of N2(e) and N2*(2D,2P) with IF.

This paper describes the excitation of IF by the nitrogen metastables present in active nitrogen—the effluents of microwave discharges in Ar/N2 or He/N2 mixtures. The intensity of the IF(B) excitation and its vibrational distribution, however, are quite different from those observed from N2(A) excitation. Our results indicate that the primary species responsible for the IF(B) excitation in the active nitrogen is not N2(A) but probably N2- (X1Σg-).

Experimental Section

The apparatus is a 2-in.-diameter discharge-flow reactor pumped by a Leybold-Heraeus Roots blower/forepump combination capable of producing linear velocities up to 5 \times 10^4 \text{ cm s}^{-1} at pressures of 1 Torr. The flow-tube design is modular (see Figure 1), with separate source, reaction, and detection sections that clamp together with O-ring joints. We have described it in detail previously.13

Discharging about 70 W of microwave power through a flowing mixture of nitrogen in argon or helium generated the active nitrogen. Reagents were then injected downstream from the primary discharge, and the resulting fluorescence was monitored downstream from the injector. A suprasil lens collected light from the center of the flow tube and focused it on the entrance slit of the monochromator, which is a 0.5-m Minuteman instrument equipped with a 1200 groove mm\(^{-1}\) grating blazed at 250 nm. A thermoelectrically cooled photomultiplier (HTV R943-02) detected photons with the aid of an SSR 1105 photon-counting rate meter interfaced to a laboratory computer system and strip-chart recorder.

The spectral system was calibrated for relative response as a function of wavelength by using a standard quartz-halogen or D2 lamp. Absolute response calibrations were made in situ by observing the air afterglow under carefully controlled conditions.16,17 IF entered the flow tube through a hook-shaped injector whose outlet orifice is coaxial with the main flow tube. This injector has a relatively large diameter (10-mm o.d.) and is Teflon coated to inhibit IF wall recombination. IF was produced in this injector by the reaction between CF3I and F atoms, the F atoms having been produced in a microwave discharge through CF4/He mixtures further upstream in the injector. We have detailed the characterization of this IF source previously.13,18

Mass-flow meters or rotameters monitored gas flow rates. All flow meters were calibrated by measuring rates of increase of pressure with time into 6.5- or 12-I flasks, by using appropriate differential pressure transducers (Validyne DP-15) that themselves

---

References:

(17) Wolf and Davis15,19 and others have interpreted the line shapes in terms of a single, homogeneous IF source. This interpretation is consistent with our experiments and we do not consider it here.
Excitation of IF(B^3Π setups) by Active Nitrogen

The underlying spectrum shows the contributions from the IF(B-X) system. The populations of these vibrational levels, therefore, can be obtained from the number density of added IF for a number of different initial N_2(B) number densities in the reactor. The N_2(B) number density was determined from the number densities in Figure 6, suggesting that N_2(B) and IF(B) share a common excitation source. Figure 3 is a composite of the IF(B) (B-X) system; all the features plotted as crosses in Figure 3 illustrate the final result of this procedure.

We fit the spectrum piecewise over three consecutive wavelength regions after first subtracting the N_2 first-positive contributions. The spectral region between 450 and 500 nm contains mostly bands of the IF(B-X) system from vibrational levels ν^0 = 3-8. The populations of these vibrational levels, therefore, can be determined fairly cleanly in this spectral region. The contributions of these levels to the spectrum at longer wavelengths will then be reasonably well determined from these values.

Over the wavelength region between 500 and 600 nm, the major vibrational levels of IF(B) contributing to the spectrum are ν^0 = 0-2. Fairly isolated bands at 533, 551, and 568 nm determine the ν^0 = 1 population reasonably well. In some instances, however, the ν^0 = 0 and 2 populations can be determined only by fitting shoulders of bands. By operating at flow conditions that optimize IF(B) emission relative to other emission systems, a good evaluation of the IF(B,ν^0 = 0) population can be obtained.

Figure 4 summarizes the population distributions determined from fits to several spectra obtained in a helium bath gas at 1.5 Torr. The vibrational distribution is well described by an 1150 K Boltzmann vibrational temperature. In an argon buffer the resulting vibrational distribution is somewhat hotter, ~2000 K. The significance of a Boltzmann distribution in terms of the dynamics of the energy transfer is unclear. In addition, such distributions are somewhat dependent on the conditions of the measurement since IF(B) vibrational relaxation by He, Ar, and N_2 is efficient. In either case, however, the IF(B) vibrational distribution is significantly more relaxed than that obtained from N_2(A) excitation of IF. This suggests that a nitrogen metastable other than N_2(A) is responsible for IF(B) excitation in active nitrogen.

**IF Excitation Rates in Active N_2.** To characterize the energy transfer between active nitrogen and IF, we have measured IF* excitation rates. The IF* will be in steady state because its lifetime (~8 μs)^2 is short compared to residence times in the observation volume. Thus, its formation and destruction rates can be equated. Neglecting IF* electronic quenching^2 gives

\[
I_{IF^*} = k_{rad}[IF^*] = k_{ex}[N_2^*][IF]
\]

where K_{ex} is the excitation rate coefficient for IF* excitation by active N_2, and k_{rad} is the IF* radiative decay rate. Equation 1 shows that without knowing the identity of the precursor for the IF* excitation, the product of the excitation rate coefficient and the number density of the precursor species can be determined.

Figure 5 illustrates one set of measurements on the variation in the intensity of the 5.0 band of IF(B-X) as a function of number density of added IF for a number of different initial N_2(B) number densities in the reactor. The N_2(B) number density was varied by changing the angle of rotation of a Ni screen in the flow and was monitored with a photometer centered at 580 ± 5 nm that previously had been calibrated against N_2(B,ν^0 = 2-12). The excitation rates determined from the slopes of the lines in Figure 5, after converting raw intensities to absolute photon emission rates and correcting for the fraction of total IF(B) emission appearing in the 5.0 band are on the order of 0.1 photon cm^-3 s^-1 per IF molecule cm^-2. These rates vary linearly with the measured N_2(B) number densities (Figure 6), suggesting that N_2(B) and IF(B) share a common excitation source. Figure 7 shows that the CF_2 and unidentified band intensities also vary

---

The excitation rates of IF(B) and the other emissions do vary with N₂(B) number density. The value derived, however, is (5.6 ± 0.4) x 10^7 s⁻¹, more than an order of magnitude greater than gas kinetic, meaning that N₂(B) is an unlikely excitation partner. The data show quite clearly, however, that the excitation rates of IF(B) and the other emissions do vary with N₂(B) number density. Apparently the metastable that excites the IF* and other emissions also is coupled collisionally to the N₂(B) state.

The observations discussed were made in 1.5 Torr of helium, 22 ms downstream from the microwave discharge, and with a Ni screen in the flow reactor. Observations in argon at much shorter transit times (~7 ms) and with no nickel screen in the reactor resulted in IF(B) excitation rates that approached unity, i.e., 1 IF(B) photon cm⁻³ s⁻¹ per IF molecule cm⁻³ in the observation region. These experiments also gave a somewhat hotter IF(B) vibrational distribution.

The larger excitation rates in argon buffer suggest that the metastable species responsible for IF(B) excitation is deactivated by collisions with the reactor walls (enhanced in the He measurements both by the longer transit time and by the much more rapid diffusion of species in He compared to Ar) as well as by collisions with the Ni screen. Argon discharges also might generate the metastables more efficiently.

Further investigations in Ar/N₂ afterglows indicated a decline in the effective IF(B) excitation rate of roughly a factor of 2 in changing the N₂ mole fraction from 0.02 to 0.90. Inserting a glass-wool plug into the flow just downstream from the discharge, however, reduced the IF(B) excitation rate to levels comparable to the noise level. The glass-wool plug quenches all electronic and most vibrational excitation in the flow but generally reduces the number density of atoms by only about 20%. We discuss the implications of these observations in the next section.

### Discussion

The maximum excitation rate of 1 photon cm⁻³ s⁻¹ per IF molecule cm⁻³ places a lower limit on the number density of the exciting species. This limit aids in identifying the metastable responsible for the IF excitation. Even if the excitation rate coefficient for the active species were gas kinetic (~10⁻14 cm³ molecule⁻¹ s⁻¹), the concentration of the exciting species could be no smaller than 10¹⁴ molecule cm⁻³. A slower excitation rate coefficient would require a more plentiful excitation partner.

Spectroscopic observations between 130 and 850 nm of the discharge effluent helped to characterize the metastable species in the flow. Prominent emissions observed 20 ms downstream from the discharge included the Lyman-Birge-Hopfield (a'Π_a-X'-Σ⁺_a), Ogawa-Tanaka-Wilkinson-Mulliken (a'Π_a-X'-Σ⁺_a), Vegard-Kaplan (A'Σ⁺_a-X'Σ⁺_a), second-positive (C'Π_a-B'Π_a), and first-positive (B'Π_a-A'Σ⁺_a) systems of N₂, the NO γ-bands (A'Σ⁺_a-X'Σ⁺_a), and N₂(P-S, λ = 346.6 nm). Under some conditions, when CF₃ was added to the reactor, the CN blue (B'Σ⁺_a-X'Σ⁺_a) and red (A'Π_a-X'Σ⁺_a) systems appeared. We have also characterized the N₂(X,ν) vibrational distributions using a Penning-ionization diagnostic and N₂(Π)

### Table I: Active Nitrogen Constituents in Argon

<table>
<thead>
<tr>
<th>species</th>
<th>observation band</th>
<th>concn, molecule cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂(Π)</td>
<td>vacuum UV resonance</td>
<td>1 x 10¹⁰</td>
</tr>
<tr>
<td>N₂(a'Π)</td>
<td>(a'Π_a-X'-Σ⁺_a)</td>
<td>4 x 10¹⁰</td>
</tr>
<tr>
<td>N₂(a'Σ⁺)</td>
<td>(a'Σ⁺_a-X'Σ⁺_a)</td>
<td>5 x 10¹⁰</td>
</tr>
<tr>
<td>N₂(B'Π)</td>
<td>(B'Π_a-A'Σ⁺_a)</td>
<td>8 x 10⁹</td>
</tr>
<tr>
<td>N₂(A'Σ⁺)</td>
<td>(A'Σ⁺_a-X'Σ⁺_a)</td>
<td>1 x 10⁹</td>
</tr>
<tr>
<td>N₂(ν)</td>
<td>He⁺ Penning ionization</td>
<td>2 x 10¹⁴</td>
</tr>
</tbody>
</table>

Further investigations in Ar/N₂ afterglows indicated a decline in the effective IF(B) excitation rate of roughly a factor of 2 in changing the N₂ mole fraction from 0.02 to 0.90. Inserting a glass-wool plug into the flow just downstream from the discharge, however, reduced the IF(B) excitation rate to levels comparable to the noise level. The glass-wool plug quenches all electronic and most vibrational excitation in the flow but generally reduces the number density of atoms by only about 20%. We discuss the implications of these observations in the next section.
Excitation of IF(B′3Πg) by Active Nitrogen

by vacuum UV resonance absorption and fluorescence.23

Table I lists estimates, based on the photon emission rate measurements and the other data, of the likely excited-state species concentrations in active nitrogen for two different compositions at 1 Torr. These estimates show that only N2(Π), N2(Δ), and N2(σ) exist in high enough concentrations to excite IF at the rates observed.

N2(Δ) and N2(σ) are unlikely precursors for IF(B) excitation. N2(Π) number densities decrease dramatically with increases in nitrogen mole fraction. The IF excitation rates, on the other hand, decreased only slightly. Because N2(Π) is quenched by Ar, this metastable tends to be more abundant in helium flows. We found, however, that IF excitation rates were somewhat greater in argon buffers.

We think the most likely excitation species is N2(X,ν>9). Extremely high levels of vibrational excitation can survive long into the afterglow because they will not be relaxed efficiently by N2, Ar, or He. Our Penning-ionization measurements indicate substantial vibrational excitation in N2(X). In some instances more than two-thirds of the N2(X) is vibrationally excited,22 and the vibrational excitation extends at least as high as 3.8 eV.21 We believe that it is these high vibrational levels of N2(X,ν) that are responsible for the excitation of N2 electronic states in the afterglow as discussed in the previous subsection. Because the measured IF excitation rates vary linearly with the N2(B) fluorescence intensity, it appears that both species are likely to be excited by the same precursor. The precursor for the N2(B) emission cannot be N2(Π) because that state lacks sufficient energy to excite N2(B). Thus N2(X,ν>9), because it is the only remaining long-lived state in the reactor, appears to be the precursor state for N2(B) excitation. This excitation could be either direct or indirect through an intermediary state of nitrogen that is excited from the N2(X,ν>9) precursor. Inserting the glass-wool plug into the active nitrogen stream eliminates vibrationally excited N2 and electronically excited atomic and molecular metastables, leaving only N2(Σg). The small residual IF excitation in this case is consistent with expected N2* number densities created by N-atom recombination.

Grigor and Phillips24 and Phillips25 have studied molecular and atomic emission in active nitrogen flames with added I2, IBr, ICI, and ICN. They observed emission from electronically excited I2 and electronically excited atomic and molecular metastables, leaving only N2(Σg). The small residual IF excitation in this case is consistent with expected N2* number densities created by N-atom recombination.

Our studies indicate that both N2(A) and N2(X,ν>9) can excite IF(B). N2(W3Δ2) might also excite IF(B), but it should not be responsible for the IF(B) excitation we observe. N2(W3Δ2) is very efficiently coupled to N2(B) in collisions with N2, Ar, and He.26,27 Its steady-state number densities, therefore, will be similar to those for N2(B), and we have shown that N2(B) is not sufficiently populated to be responsible for the IF(B) excitation that we observe.

In a limited-distribution report, West and Bhaumik28 related observations of IF(B) fluorescence when they added IF or just CF3I to a flow of active nitrogen. Their active nitrogen was prepared by discharging pure nitrogen at relatively high pressures, 5–20 Torr. They showed that the intensity of IF(B) they observed was proportional to the number density of atomic nitrogen. The nitrogen species exciting their IF(B), therefore, was generated from N-atom recombination. They suggested N2(σ) as the exciting species, but given the steady-state number densities of N2(σ) they calculated to be in their system and the efficiency we determined for IF(B) excitation by N2(σ), their observations are fully compatible with N2(σ) as the excitation source.

More recently, Ongstad et al.29 observed IF fluorescence generated by the addition of CF3I to active nitrogen. They showed that the active nitrogen dissociated the CF3I to produce F atoms, with IF generated subsequently in the reaction between F and CF3I. Inserting a glass-wool plug into their afterglow, downstream from the nitrogen discharge but upstream from the CF3I inlet, had little effect on their observed IF(B) intensities. Here again, the excited nitrogen molecules that pumped IF(B) were generated by N-atom recombination. In such a case one cannot distinguish between N2(A) and N2(X,ν) as the excitation source.

Davis30 has shown that a steady-state number density of IF(B) of 1014 molecules cm−3 will be sufficient to achieve an optical gain of 0.1% cm−1. A gain of this magnitude would render laser oscillation easily achievable. Our conditions of relatively mild N2 excitation, low ground-state IF number density (~1011 molecules cm−3), and low total pressure (~1 Torr) produces steady-state IF(B) number densities of 109 molecules cm−3. An increase of at least 4 orders of magnitude in IF(B) number density ought to result from easily achieved increases in total pressure and ground-state IF number density. Additional enhancement of the IF(B) number density would require improved N2* production. This might be accomplished by a higher power excitation source. The phenomenon known as V−V up pumping31,32 allows substantial number densities of highly vibrationally excited N2 to be produced by appropriate discharge sources. This is in contrast to N2(A2Σg+), whose maximum number densities will be limited by energy-pooling reactions.33,34 The interaction between N2(X,ν) and IF therefore shows some promise as a potential chemical laser source.

Acknowledgment. We appreciate financial support from the Air Force Weapons Laboratories under Contract No. F-29601-83-C-0051 and F29601-84-C-0076. We also appreciate the helpful comments of our PSI colleagues Terry Rawlins, Dave Green, Steve Davis, and George Caledonia.

Registry No. N, 17778-88-0; IF, 13873-84-2; N2, 7727-37-9.